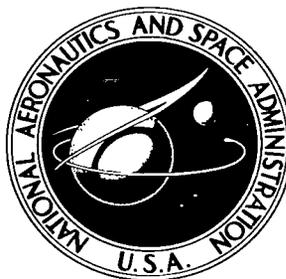


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# STRESS-CORROSION CRACKING OF Ti-6Al-4V TITANIUM ALLOY IN NITROGEN TETROXIDE

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# STRESS-CORROSION CRACKING OF Ti-6Al-4V TITANIUM ALLOY IN NITROGEN TETROXIDE

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## SUMMARY

The stress-corrosion of Ti-6Al-4V titanium alloy in nitrogen tetroxide was investigated by using small laboratory-size self-stressed specimens and tanks. Tests were conducted from 65° F to 165° F (290° K to 345° K) for purposes of determining the time for crack initiation. At 165° F (345° K) the cracking was severe and resulted in failures within 4 hours exposure, the damage diminishing rapidly with decreasing temperature. At 75° F (295° K), no stress-corrosion damage was observed for exposures up to 500 hours. Stress levels from 25 to 100 ksi (170 to 690 MN/m<sup>2</sup>) were investigated and crack initiation was observed at all stress levels in approximately the same time. An excellent correlation was obtained between crack initiation time on laboratory specimens and failure time for tanks.

Tests were also conducted on specimens which had been treated in some manner for the prevention of stress-corrosion attack. Organic and metallic coatings investigated proved to be unsatisfactory because of adherence problems or apparent permeation resulting in stress-corrosion attack. Surface treatments including peening techniques proved to be beneficial and glass-bead peening to introduce residual compressive stresses of high magnitude appeared to alleviate the problem entirely for the range of tests conducted. The residual stress level was determined by X-ray diffraction techniques and was found to be in excess of 100 ksi (690 MN/m<sup>2</sup>) on the surface. The prevention of stress-corrosion attack by chemical inhibition with 0.78 percent by mass nitric oxide (NO) added to the N<sub>2</sub>O<sub>4</sub> was also substantiated by tests conducted at 165° F (345° K) for exposures of 170 hours. The mechanism of prevention remains unknown.

## INTRODUCTION

The Ti-6Al-4V titanium alloy in the solution-treated and aged condition is used as a structural material for liquid propellant tanks in many current aerospace vehicles because of its favorable strength-weight ratio and relative chemical inertness to highly corrosive liquid propellants. Recent experience, however, indicated that Ti-6Al-4V

titanium-alloy tanks showed evidence of stress-corrosion damage when exposed to nitrogen tetroxide ( $N_2O_4$ ) under pressure (ref. 1).

Because this problem affected many tanks currently in existence, an investigation was undertaken to obtain information on the nature of the stress-corrosion problem and to determine protective treatments which would make it possible to utilize the many existing propellant tanks. This paper presents the results of stress-corrosion tests of small self-stressed specimens at levels from 25 to 100 ksi (170 to 690  $MN/m^2$ ) exposed to four different  $N_2O_4$  oxidizers and different temperatures. Also presented are the results of tests on three tanks made to correlate specimen data with actual hardware data. The correlation obtained between tests on small specimens and tanks is shown, and the effectiveness of various protective treatments such as coatings, additions to the oxidizer, and various peening techniques is described.

A concurrent study was also carried out on the development of parameters necessary topeen with glass beads the internal surface of full-scale tanks as a possible solution to the stress-corrosion problem. Results of the investigation on tank parameter development can be found in reference 2.

The units used for the physical quantities in this paper are given both in the U.S. Customary Units and the International System of Units (SI) (ref. 3). The conversion factors required for units in the present study are presented in the appendix.

## SPECIMENS AND MATERIALS

### Self-Stressed Specimens

Small self-stressed specimens of the type described in reference 4 were constructed from 1/4-inch- (0.64 cm) wide by 4-inch- (10 cm) long strips of 0.04-inch- (0.10 cm) thick Ti-6Al-4V titanium-alloy sheet in the annealed condition. The ends of the strips were preformed as shown in figure 1(a) and then spotwelded together (fig 1(b)) to induce a uniform bending stress in the curved portions of the specimen. The preformed bend angle in the specimen determines the amount of curvature and thus the magnitude of the outer fiber stress in the specimen. The specimens were designed with maximum tensile stresses on the outer fiber of 25, 50, 75, and 100 ksi (170, 340, 520, 690  $MN/m^2$ ).

Several treatments were applied to these specimens to investigate possible prevention of the corrosion attack. These treatments consisted either of a coating or mechanical treatment and are described as follows:

The coatings which were investigated included an aluminum coating which was deposited by a chemical vapor deposition process, a polytetrafluoroethylene tape coating which was tightly wrapped on the specimens, and a special polymer coating of the

"pyrrone" family. In each of these cases, the specimens were in the stressed condition before application of the coating.

The mechanical surface treatments which were investigated included vibratory and glass-bead peening to obtain a uniform continuous cold worked layer on the surface of the material. In each of these processes the flat strips for preparation into specimens were treated prior to stressing, a condition more closely simulating actual applied procedures. In the vibratory process the flat strips were placed in a container with small abrasive alumina triangles and vibrated at an amplitude of approximately 0.1 inch (0.25 cm) at 1450 cycles per minute (24 Hz) for approximately 24 hours. The glass-bead peening process consisted of bombarding the material with small glass spheres of 0.007-inch diameter (0.18 mm) propelled through a nozzle by pressurized air.

### Tanks

The cylindrical tanks with hemispherical ends were fabricated of Ti-6Al-4V titanium alloy cylindrical and hemispherical forgings 0.5 inch (1.25 cm) thick in the solution-treated and aged condition. The forgings were machined to final dimensions with a wall thickness which ranged from 0.020 to 0.025 inch (0.051 to 0.064 cm) and then joined by tungsten inert gas welding. The tanks contained no longitudinal welds. The tanks included in the investigation ranged from 24 to 29 inches (61 to 74 cm) in length and were 12.5 inches (32 cm) in diameter. (See table I.)

TABLE I. - TEST CONDITIONS AND RESULTS OF Ti-6Al-4V TITANIUM-ALLOY TANKS CONTAINING N<sub>2</sub>O<sub>4</sub>

Tank size				Type of oxidizer	Surface treatment	Exposure time, hr	Exposure temperature		Test pressure		Nominal hoop stress		Type failure
Diameter		Length					°F	°K	psi	MN/m <sup>2</sup>	ksi	MN/m <sup>2</sup>	
in.	cm	in.	cm										
12.5	32	<sup>a</sup> 29	74	A	None	115	105	315	250	1.72	90	620	Leak
12.5	32	<sup>b</sup> 24	61	A	Vibratory peened	200	105	315	250	1.72	90	620	Leak
12.5	32	<sup>a</sup> 29	74	A	Glass-bead peened	720	105	315	250	1.72	90	620	None

<sup>a</sup>Apollo service-propulsion-system reaction-control oxidizer tank.

<sup>b</sup>Apollo service-propulsion-system fuel tank.

One of the tanks was vibratory peened and another glass-bead peened in the same manner as the self-stressed specimens. The vibratory-peened tank was filled approximately one-third full with the abrasive media and vibrated again at an amplitude of 0.1 inch (0.25 cm) at approximately 1450 cycles per minute (24 Hz). The tank was peened for 72 hours and rotated about its longitudinal axis 45° every 8 hours. The glass-bead-peened tank was treated by rotating the tank on a cradle around a single

nozzle which was positioned inside the tank and moved along the cylindrical axis. The peening equipment was of the suction type and the overall process is more completely described in reference 2.

### Oxidizer

The nitrogen tetroxide utilized in this investigation was procured from four different sources (table II) for purposes of investigating effects of variation in batches or lots. Oxidizers A, B, and C were prepared under the existing military specification for its preparation. Oxidizer A was procured in a large quantity (2000 lbm (900 kg)) of a given lot and oxidizer B was a smaller quantity (100 lbm (45 kg)) of a different lot. Oxidizer C was obtained from the storage facilities at Kennedy Space Center to obtain additional data from an oxidizer lot planned for use in current launch vehicles. Oxidizer D was specially prepared with a high nitric oxide content (0.78 percent by mass) added as a corrosion inhibitor. Prior to the inception of this study, all nitric oxide was being removed from  $N_2O_4$  in the final manufacturing process of oxygenation. In preliminary experiments it was found that the presence of nitric oxide in  $N_2O_4$  can be detected by a characteristic "green" color when the  $N_2O_4$  is frozen. A similar color is also obtained if  $N_2O_4$  contaminated with water is frozen. Nitrogen tetroxide that does not contain either nitric oxide or water displays a white or straw color when frozen.

TABLE II - COMPOSITION OF NITROGEN TETROXIDE  
[Percents given on a mass basis]

Supplier	Designation	Source of analysis	Color upon freezing	Nitrogen tetroxide, percent	Nitric oxide, percent	Chloride as NOCl, percent	Water equivalent, percent	Nonvolatile ash, g/m <sup>3</sup>
Allied	<sup>1</sup> A	NASA Wallops Station	White	99.70	Not analyzed	0.050	0.0146	Nil
Boeing	<sup>1</sup> B	Hercules Powder Company	White	99.75	Not analyzed	.135	.08	2.9
Hercules	D	Hercules Powder Company	Green	100.37	0.78	.01	.05	2.0
Kennedy Space Center	<sup>1,2</sup> C	-----	White	-----	-----	-----	-----	--

<sup>1</sup>Prepared to meet analysis under military specification.

<sup>2</sup>Procured from general pad storage.

## EQUIPMENT AND PROCEDURES

### Test Cell

A test cell was constructed which would permit the testing of both laboratory stress-corrosion specimens and full-scale tanks at high pressures in nitrogen tetroxide. The test cell consisted of a blockhouse which housed the instrumentation and equipment necessary for conduction of tests. A plan view of the test cell is shown in figure 2 and a

photograph of the installation is shown in figure 3. Four pressure vessel test cubicles for self-stressed specimens and two test cubicles for tanks were constructed. The walls of the cubicles were fabricated from 1/4-inch (0.64 cm) steel plate to provide safety from explosion to the operating personnel. Masks with built-in air supplies were used by personnel when servicing the test vessels or tanks.

### Self-Stressed Specimens

After fabrication the specimens were supported on titanium racks and placed in pressurized test vessels shown schematically in figure 4. The liquid level of the oxidizer in the pressure vessels was monitored with a liquid level gage and the vessels were heated with tape heaters insulated with glass cloth. Temperature of the test was continuously controlled and monitored by using stainless-steel-sheathed iron-constantan thermocouples and an off-on proportional controller. The thermocouples were immersed in the  $N_2O_4$  liquid at different levels and the temperature difference was found to be negligible. The vessels were pressurized to the desired test pressure with helium and monitored with pressure transducers. Photographs of the specimen test vessel setup and instrumentation are shown in figures 5 and 6, respectively.

The titanium racks were designed to hold 24 specimens but each exposure was usually limited to 12. Generally, untreated specimens of 25-, 50-, 75-, and 100-ksi (170, 340, 520, and 690  $MN/m^2$ ) stress levels were included in each exposure along with specimens which had been treated for prevention of corrosion; however, these treated specimens were limited to the 100-ksi (690  $MN/m^2$ ) stress level. Constant-temperature exposures were made from 65° F to 165° F (290° K to 345° K) for times from 3 hours to 15 days. Duplicate specimens were tested to provide some check on specimen irregularities. A typical test sequence consisted of inserting the rack with specimens into the empty vessel, sealing the vessel, and purging with helium. The vessel was then filled with the desired lot of  $N_2O_4$ , the vent sealed, and the system pressurized and then heated to the desired test temperature. During heating, pressure was limited by the pressure relief valve. Test start time was taken as the moment when the system reached test temperature and test stop time was taken as the moment when the heating was terminated. Lag time from insertion of specimens to arrival at the test temperature was generally about 30 minutes; lag time from test stop to removal of specimens was generally less than 10 minutes. After each test, the  $N_2O_4$  was drained and discarded.

After exposure in  $N_2O_4$ , the specimens were removed and tested in axial compression in a hydraulic testing machine in the manner described in reference 4. The axial shortening and compressive load were monitored to fracture. The magnitude of the axial shortening that a specimen exhibits at fracture is labeled  $\delta$  and is termed the absolute deflection. In figure 1(c) the specimen which has not experienced any stress corrosion has been deformed a value  $\delta_0$  prior to fracture and in figure 1(d) the

specimen containing stress-corrosion cracks has deflected a value  $\delta$  prior to fracture. The stress-corrosion damage of self-stressed specimens is hence related to the relative deflection  $\delta/\delta_0$ .

For specimens which underwent a surface treatment for the introduction of residual compressive stresses, an X-ray diffraction technique was used for the determination of the stress levels achieved. The technique of measuring residual stress by X-ray diffraction involves measuring the change in atomic spacing on a given set of atomic planes oriented at two different angles with respect to the plane of the specimen. The residual stress measured is considered an average stress for a surface layer of approximately 0.0005 inch (13  $\mu\text{m}$ ) thick. In order to determine the effective depth of the residual stresses, layers of material approximately 0.0005 inch (13  $\mu\text{m}$ ) were chemically milled from the sheet and stress measurements were made after each layer was removed by using the X-ray diffraction technique. Details of this procedure can be found in reference 5.

### Tank Tests

A sketch of a tank under test in a metal box is shown in figure 7 and a photograph in figure 8. The metal box was located in a tank cubicle and both were insulated on the sides and top. The tanks were positioned over a stand pipe which afforded means for pressurization of the system. On each tank four thermocouples were tack-welded on the seam welds. One of the two thermocouples located on the lower seam was used to control the system temperature and the other three thermocouples were continuously recorded on a strip chart recorder. In addition, two stainless-steel-sheathed thermocouples were immersed in the liquid to monitor the liquid temperature and the temperatures were continuously recorded. The tanks were instrumented with five foil-type strain gages bonded to the tank outer surface. These gages were used to measure dome strain, and longitudinal and hoop strain in the cylindrical section. Pressure in the tank was controlled by using a two-stage pressure regulator and was continuously monitored with a pressure transducer. The desired test temperature was achieved with the aid of 12 strip heaters mounted within the metal box. The amount of  $\text{N}_2\text{O}_4$  in the system was controlled with liquid level gages which were located outside the cubicle for safe monitoring. The same oxidizer (oxidizer A) was used for each of the tank tests.

A typical test sequence for the tank testing is as follows: The tank was positioned in the metal box and then purged and pressurized with helium to 100 psi (690  $\text{kN/m}^2$ ). The tank was then checked for leaks to assure a leak-tight system. The metal box was then closed and the tank was vented and filled with oxidizer to the desired level. The tank was again sealed and heating to the desired test temperature was begun. After the test temperature was achieved, pressurization with helium was accomplished in 25-psi

(173 kN/m<sup>2</sup>) increments to 250 psi (1.72 MN/m<sup>2</sup>) and resulted in a nominal hoop stress of 90 ksi (620 MN/m<sup>2</sup>). This procedure was used to prevent overheating the tank through pressurization. The startup procedure required approximately 2 hours. The test start time was taken as the time at which test pressure was achieved and test stop time was taken as the time at which test pressure was reduced to ambient. After termination of the exposure test, the N<sub>2</sub>O<sub>4</sub> was drained and discarded, the tanks were removed, washed, and examined for evidence of damage.

The tank that was peened with glass beads was pressurized with water to failure to determine burst pressure after long-time exposure to N<sub>2</sub>O<sub>4</sub>. Test pressure rise rate was approximately 50 psi (345 kN/m<sup>2</sup>) per minute.

## RESULTS AND DISCUSSION

### Untreated Self-Stressed Specimens

The variables influencing the magnitude of the stress corrosion in the Ti-6Al-4V titanium alloy-N<sub>2</sub>O<sub>4</sub> system that are considered to be important are time, temperature, and stress level. Alteration of any or all of these variables may alleviate the problem or eliminate it. The tests in this study were conducted to provide adequate data on the important variables influencing the stress-corrosion problem.

Effect of stress, temperature, and time.- The results of stress-corrosion tests on self-stressed specimens exposed at 165° F (345° K) are shown in figure 9. As noted previously, all tests conducted to investigate time-temperature effects were made with the same lot of nitrogen tetroxide oxidizer (type A, table II) to eliminate the effect of possible variations in composition of the oxidizer. In figure 9, relative deflection is plotted against exposure time; relative deflection for no damage, where  $\delta/\delta_0 = 1$ , is established from tests on unexposed specimens. The symbols  $\delta$  and  $\delta_0$  are defined in figure 1. The two curves shown define the upper and lower limits of the data. The different symbols indicate the tensile stresses in the outer fibers before exposure to N<sub>2</sub>O<sub>4</sub>. These data do not show any systematic variation with stress. One of the most useful results obtained from this figure is the determination of the time required to initiate measurable stress-corrosion damage. In figure 9 stress-corrosion damage became significant (as detected by a change in the relative deflection of the self-stressed specimens under axial loading) after about 4 hours at 165° F (345° K).

Stress-corrosion data from exposures at 145° F (335° K) are presented in figure 10. These data show similar trends to those observed in figure 9. The effect of different stresses in the range from 25 to 100 ksi (170 to 690 MN/m<sup>2</sup>) is again similar to the results obtained at 165° F (345° K). The time to initiation of measurable stress-corrosion damage was taken to be about 7 hours for exposure at 145° F (335° K).

A few tests were made at 125° F (325° K) to define the time to initiation of measurable stress-corrosion damage. This time was estimated from the tests to be 20 hours. Figure 11 shows the result of exposure at 105° F (315° K). The time to initiation of measurable stress-corrosion damage is slightly greater than 50 hours.

The lowest test temperature at which stress-corrosion damage was found to occur in this investigation was 85° F (300° K), and the results are shown in figure 12. The time to initiation of measurable stress-corrosion damage is estimated at 120 hours. Again, no consistent trend with stress level is apparent. Some tests were conducted at 65° F and 75° F (290° K and 295° K) for up to 500 hours test time with no observed evidence of stress-corrosion damage.

A cross-sectional view of a typical specimen showing the type of stress-corrosion cracks that developed is given in figure 13. The edge of the specimen is shown. The cracks contain numerous branches and are both transgranular and intergranular. This specimen was tested at 165° F (345° K) for 8 hours at a stress level of 100 ksi (690 MN/m<sup>2</sup>). Similar cracks developed in the specimens at the lower test temperatures and lower stress levels.

Figure 14 summarizes the results of the stress-corrosion tests in terms of temperature plotted against time to initiation of measurable stress-corrosion damage. The symbols indicate the time and temperature for which crack initiation was estimated. These results define a stress-corrosion threshold boundary. To the left of the boundary, no stress corrosion or damage evidenced by decreases in relative deflection was detected; to the right, stress-corrosion cracks developed rapidly and specimen fracture during exposure was possible.

Reduction of the test temperature from 165° F to 85° F (345° K to 300° K) showed a significant increase in time to initiation of measurable stress-corrosion cracking. Extensive stress-corrosion damage at 105° F (315° K) occurred under 100 hours exposure.

Effect of corrosive media variations.- The results of the tests conducted in different samples of nitrogen tetroxide are shown in figure 15. The threshold data for 165° F (345° K) of figure 9 which were determined from tests using oxidizer A are reproduced in the figure along with the data from tests using oxidizers B, C, and D. Oxidizers A, B, and C were all procured under the same military specification. Tests conducted in oxidizer B provided data which fell to the right of the damage band defined in the threshold tests whereas tests conducted in the oxidizer C provided data that fell to the left of the damage band. Although these results did show variations with different samples of oxidizer, the magnitude of the variations is not surprising for such time-dependent phenomena. This result suggests that a minor chemical difference may affect the stress-corrosion attack.

Also included in figure 15 are data from tests conducted in oxidizer D which was chemically inhibited with nitric oxide. These tests were conducted to determine the effectiveness of this inhibitor in the prevention of stress-corrosion attack. Preliminary tests (ref. 1) indicated that additions from 0.45- to 0.85-percent nitric oxide content successfully prevented stress-corrosion attack for the exposure times of the investigation. The data shown in figure 15 for the present investigation indicate that no stress-corrosion attack was observed for 170 hours exposure at 165<sup>o</sup> F (345<sup>o</sup> K). On the basis of these tests the addition of NO to N<sub>2</sub>O<sub>4</sub> appears to prevent stress corrosion of the Ti-6Al-4V. No long-time tests have been conducted beyond the 170-hour exposure. The mechanism for alleviation of the corrosion is unknown and warrants further study.

#### Treated Self-Stressed Specimens

Protective treatments can be categorized either as those involving external protection such as obtained with coating systems or as processes involving alteration of the tankage material itself as in surface treatment. Any coating system, if effective, will alleviate the problem by preventing contact of the corrosive media with the material being tested. Surface treatment of the material, such as those obtained by peening techniques, prevent the stress-corrosion attack by lowering or removing the applied stress on the surface of the material in contact with the corrosive media. This condition is obtained by introducing a residually stressed layer in compression by uniform cold working to counteract the applied tensile stress.

Surface coatings.- The tests on specimens protected with polytetrafluoroethylene tape resulted in stress-corrosion cracking beneath the tape that indicated that the liquid penetrated the wrapped layers. This coating material applied directly on the surface was investigated by others (ref. 1) and was found to be unreliable and difficult to apply to the inner surfaces of tanks. For this reason, no further work was done on this system. The polymer coating provided protection against stress corrosion for short time exposure (100 hours), but visual examination indicated a general attack of the oxidizer on the coating itself which apparently resulted in spalling of the coating or actual dissolving of the coating into the liquid. Either of these occurrences might be prohibitive from a performance standpoint even if the coating prevented attack for the required length of time. Results of tests on the vapor-deposited aluminum coating indicated that penetration of N<sub>2</sub>O<sub>4</sub> through the coating was occurring or that cracks in the coating itself allowed stress-corrosion attack to occur. Specimens failed in approximately the same time as untreated specimens with one exception. One specimen was unattacked after 100 hours exposure at 165<sup>o</sup> F. None of the coatings investigated appeared to be suitable for prevention of the stress-corrosion attack of this alloy in N<sub>2</sub>O<sub>4</sub>.

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Surface treatments. - The results of tests on specimens which had been vibratory peened showed that the process was unreliable and was effective for stress-corrosion prevention in only about half of the tests conducted. The protection mechanism involved here may be the removal of surface defects as well as introducing a residually stressed compressive layer on the surface of the material. X-ray diffraction analysis indicated that the magnitude of the compressive stress was only 35 ksi (240 MN/m<sup>2</sup>) which appears to be 65 ksi (450 MN/m<sup>2</sup>) less than the 100 ksi (690 MN/m<sup>2</sup>) applied tensile stress of the test specimens. However, the measured stress is an average value for an X-ray penetration of approximately 0.0005 inch (13 μm) and the magnitude of the surface stress may actually approach a value of 100 ksi (690 MN/m<sup>2</sup>). If this level of stress existed, it would be an extremely thin layer, would be subject to localized damage during handling, and would allow corrosion to begin at these damaged sites. Therefore, the poor reliability of this process could be due to the lack of penetration of the peening.

Specimens which were peened with glass bead for the purpose of introducing a greater compressive surface stress to a deeper level of penetration than was achieved by the vibratory treatment provided better results. This method was utilized (ref. 6) for the alleviation of hot-salt stress corrosion and some improvement was noted. However, some stress-corrosion attack occurred after extended exposure times. This result may be attributable to yielding at the 600° F exposure. For the lower temperatures associated with the N<sub>2</sub>O<sub>4</sub> stress corrosion, it appeared that a higher residual surface stress level could be maintained.

X-ray diffraction analyses indicated that the residual stress on the outer surface was greater than 100 ksi (690 MN/m<sup>2</sup>). The results of the determination of the residual stress at various depths beneath the outer surface are shown in figure 16. These data indicate that the peening process produces a surface layer compressively stressed above 100 ksi (690 MN/m<sup>2</sup>) which is greater than the nominal 100-ksi (690 MN/m<sup>2</sup>) stress in the self-stressed specimens. Compressive stresses of reduced magnitude extended from the surface to nearly 0.0035 inch (0.01 cm) below the surface.

The results of the corrosion tests on peened specimens at 165° F (345° K) are shown in figure 17, along with data on untreated specimens for comparative purposes. The test results indicate that the glass-bead peening alleviated the stress-corrosion problem for the range of conditions of the investigation. The corrosion tests of peened specimens at other temperatures produce similar results. Approximately 100 peened specimens were tested and only one specimen failed. This failure occurred outside the test section of the specimen in the bend transition region.

## Tanks

One tank filled with  $N_2O_4$  (oxidizer A, table I) was tested in the as-received condition for base line data and failed after approximately 115 hours by leaking. Examination of the tank after the test showed no evidence of extensive corrosion cracks but indicated a single crack which produced the leak. This type of failure is characteristic of the failures reported by other investigators in similar tests on titanium-alloy tanks.

The results of this tank test and unpublished test results obtained from similar untreated tanks by other investigators are shown in figure 18. The data obtained from the small self-stressed specimens which provided the curve of figure 14 are also included. It is interesting to note that the failures of the tanks with two exceptions all appear to the right of the curve labeled "Initiation of stress-corrosion damage." It appears that the initiation of cracks in the self-stressed specimens provides a reasonable guide to the prediction of stress-corrosion damage in the tanks. The correlation is excellent in spite of the fact that the titanium-alloy sheet material in the small specimens was in the annealed condition and the tanks were fabricated from the same alloy in the solution-treated and aged condition. The results suggest that this heat treatment or lack of heat treatment will not strongly influence  $N_2O_4$  stress corrosion for the conditions examined.

Another consideration is that the data from the self-stressed specimens represent uniaxial tensile conditions whereas the data from the tanks were obtained from material stressed in the biaxial condition. Apparently, in this case, the extent of the stress corrosion in  $N_2O_4$  is not sensitive to the different stress conditions.

The second tank test involved the tank which was treated with the vibratory peening process and failed after approximately 200 hours exposure in  $N_2O_4$  (table I, oxidizer A) in the same manner as the first tank failure. However, the increase in exposure time before failure was significant in comparison with the failure time (120 hours) of the untreated tank, and indicated some delay in the stress-corrosion attack resulting from the vibratory peening process. The test conditions shown in table I indicate a hoop stress of 90 ksi ( $620 \text{ MN/m}^2$ ). The induced residual surface stress was 35 ksi ( $240 \text{ MN/m}^2$ ) in compression as measured by X-ray diffraction techniques and represents an average stress for 0.0005-inch ( $13 \mu\text{m}$ ) penetration. The same general conclusions can be made as were discussed for the self-stressed specimens.

In the third test the glass-bead-peened tank was exposed for 30 days (720 hours) to  $N_2O_4$  (oxidizer A, table I) by using the same conditions as in the previous tank tests and no evidence of stress-corrosion damage was detected. The tank was then subjected to an internal pressure test to determine rupture pressure. The tank failed at a pressure of 545 psi ( $3.76 \text{ MN/m}^2$ ), a value approximately equal to the burst pressure for untreated and unexposed tanks. This result is significant because it indicated that the combined effects of the peening process and the subsequent 30-day exposure did not measurably

alter the material properties of the tank. Because of the effectiveness of the glass-bead peening in protecting Ti-6Al-4V alloy against stress corrosion in  $N_2O_4$ , equipment was designed and processes developed for controlled glass-bead peening of spacecraft tanks (ref. 2).

#### CONCLUDING REMARKS

An investigation was undertaken to determine effects of time, temperature, and stress on the stress corrosion of Ti-6Al-4V titanium alloy in  $N_2O_4$  and to develop possible methods for alleviating the corrosion. The following conclusions are based on the results of the investigation:

Stress-corrosion cracking of Ti-6Al-4V titanium alloy in liquid  $N_2O_4$  was demonstrated from tests of small self-stressed corrosion specimens and tanks. Results from corrosion tests of small specimens appear to correlate well with corrosion tests of tanks. The time required for crack initiation of the specimens was determined for temperatures from  $85^\circ F$  to  $165^\circ F$  ( $300^\circ K$  to  $345^\circ K$ ) and stresses from 25 to 100 ksi ( $170$  to  $690 MN/m^2$ ). Tests conducted on specimens at  $65^\circ F$  and  $75^\circ F$  ( $290^\circ K$  and  $295^\circ K$ ) showed no evidence of attack for exposures up to 500 hours. There was little effect of applied stress on the time required for crack initiation.

The metallic and organic coatings investigated were found to be unsatisfactory for protecting Ti-6Al-4V alloy against stress corrosion, but surface-induced residual compressive stresses produced by glass-bead peening were found to be effective.

The magnitude of stress-corrosion damage appears to vary with chemical composition and source of oxidizer. Nitrogen tetroxide containing 0.78 percent by mass nitric oxide did not produce any stress corrosion in small test specimens.

Langley Research Center,  
National Aeronautics and Space Administration,  
Langley Station, Hampton, Va., May 17, 1967,  
129-03-07-04-23.

## APPENDIX

### CONVERSION OF U.S. CUSTOMARY UNITS TO SI UNITS

The International System of Units (SI) was adopted by the Eleventh General Conference on Weights and Measures, Paris, October 1960, in Resolution No. 12 (ref. 3). Conversion factors for the units used herein are given in the following table:

Physical quantity	U.S. Customary Unit	Conversion factor (*)	SI Unit
Length . . . . .	in.	0.0254	meters (m)
Temperature . . . . .	(°F + 460)	5/9	degrees Kelvin (°K)
Stress . . . . .	psi = lbf/in <sup>2</sup>	6895	newtons/meter <sup>2</sup> (N/m <sup>2</sup> )
Pressure . . . . .	psi = lbf/in <sup>2</sup>	6895	newtons/meter <sup>2</sup> (N/m <sup>2</sup> )
Frequency . . . . .	cycles/minute	0.0167	Hertz
Mass . . . . .	lbm	0.4536	kilograms

\* Multiply value given in U.S. Customary Units by conversion factor to obtain equivalent value in SI Unit.

Prefixes to indicate multiples of units are as follows:

Prefix	Multiple
micro ( $\mu$ )	$10^{-6}$
milli (m)	$10^{-3}$
centi (c)	$10^{-2}$
kilo (k)	$10^3$
mega (M)	$10^6$

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4. Heimerl, G. J.; and Braski, D. N.: A Stress Corrosion Test for Structural Sheet Materials. Mater. Res. Std., vol. 5, no. 1, Jan. 1965, pp. 18-22.
5. Christensen, A. L.; Koistinen, D. P.; Marburger, R. E.; Semchyshen, M.; and Evans, W. P.: The Measurement of Stress by X-Ray. TR-182, Soc. Automotive Engrs., 1960.
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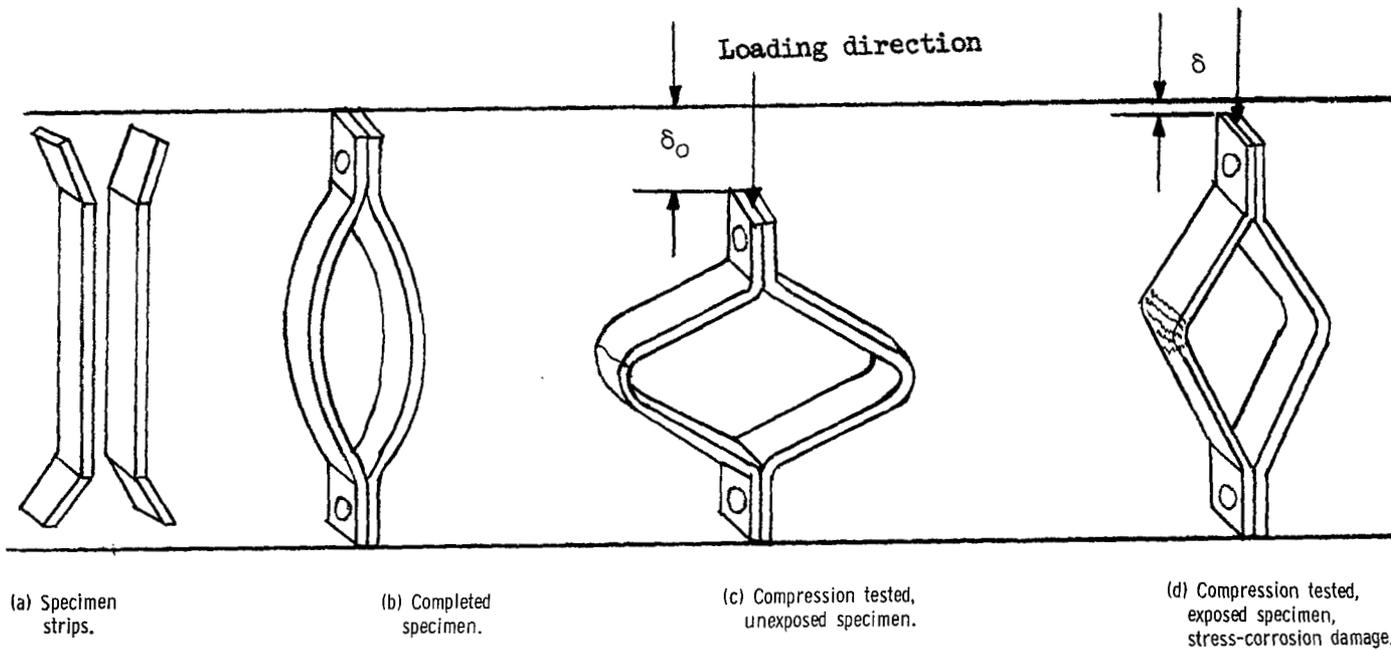


Figure 1.- Construction of self-stressed corrosion specimen, and effect of axial compression on shortening of specimens with and without stress-corrosion damage.

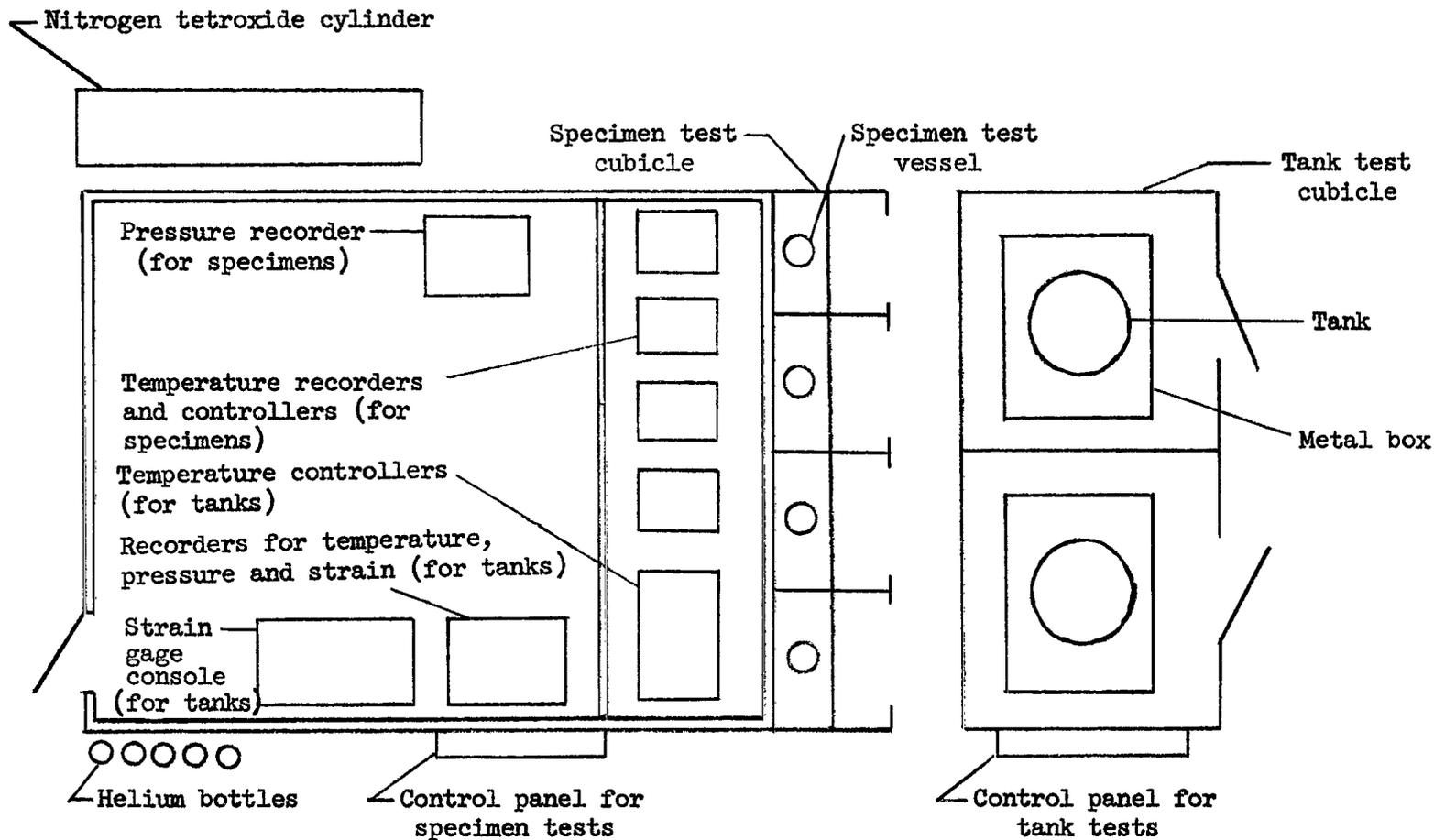


Figure 2.- Plan view of nitrogen-tetroxide stress-corrosion test cell.

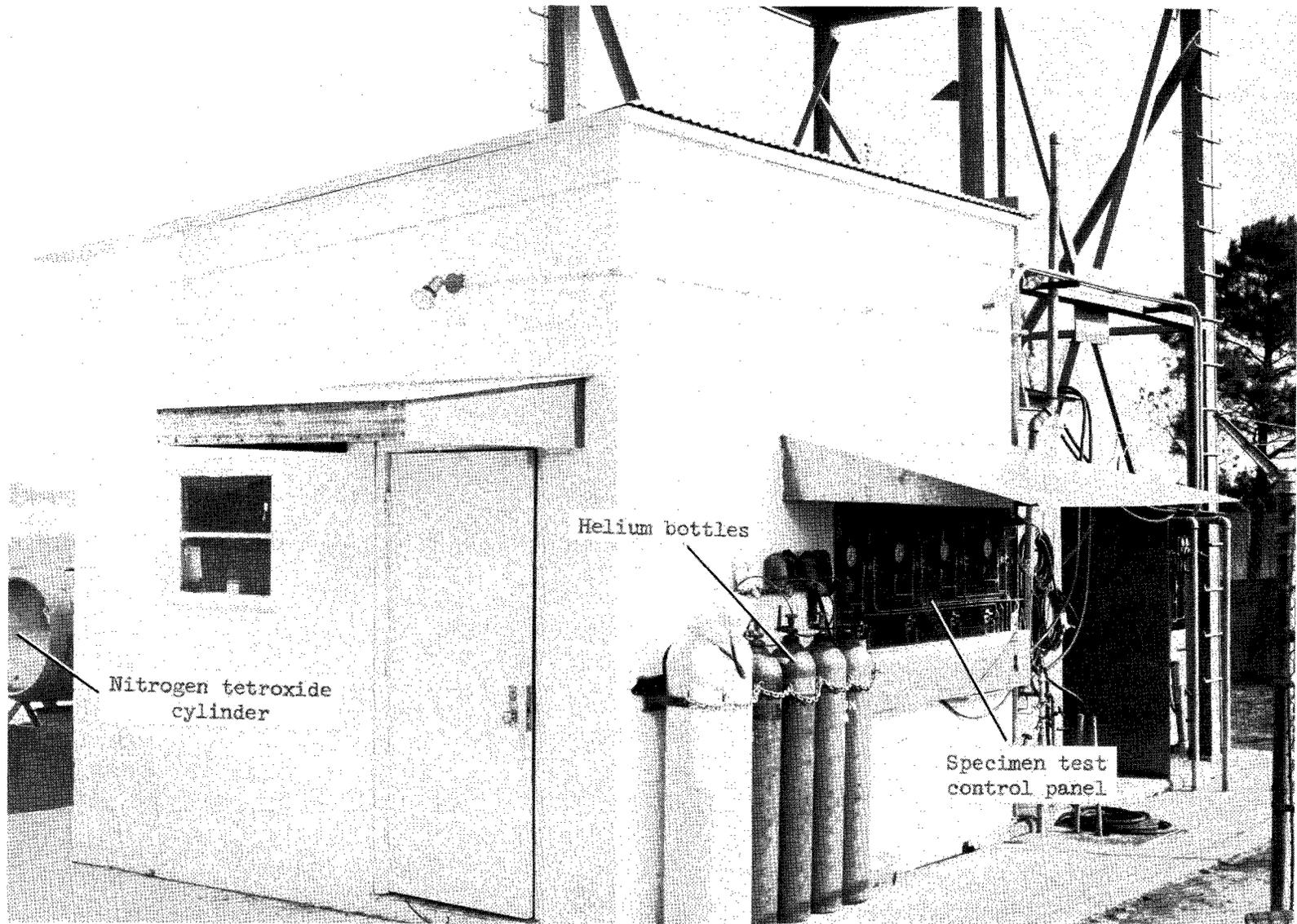


Figure 3.- Test cell for conducting tests on titanium alloy in nitrogen tetroxide.

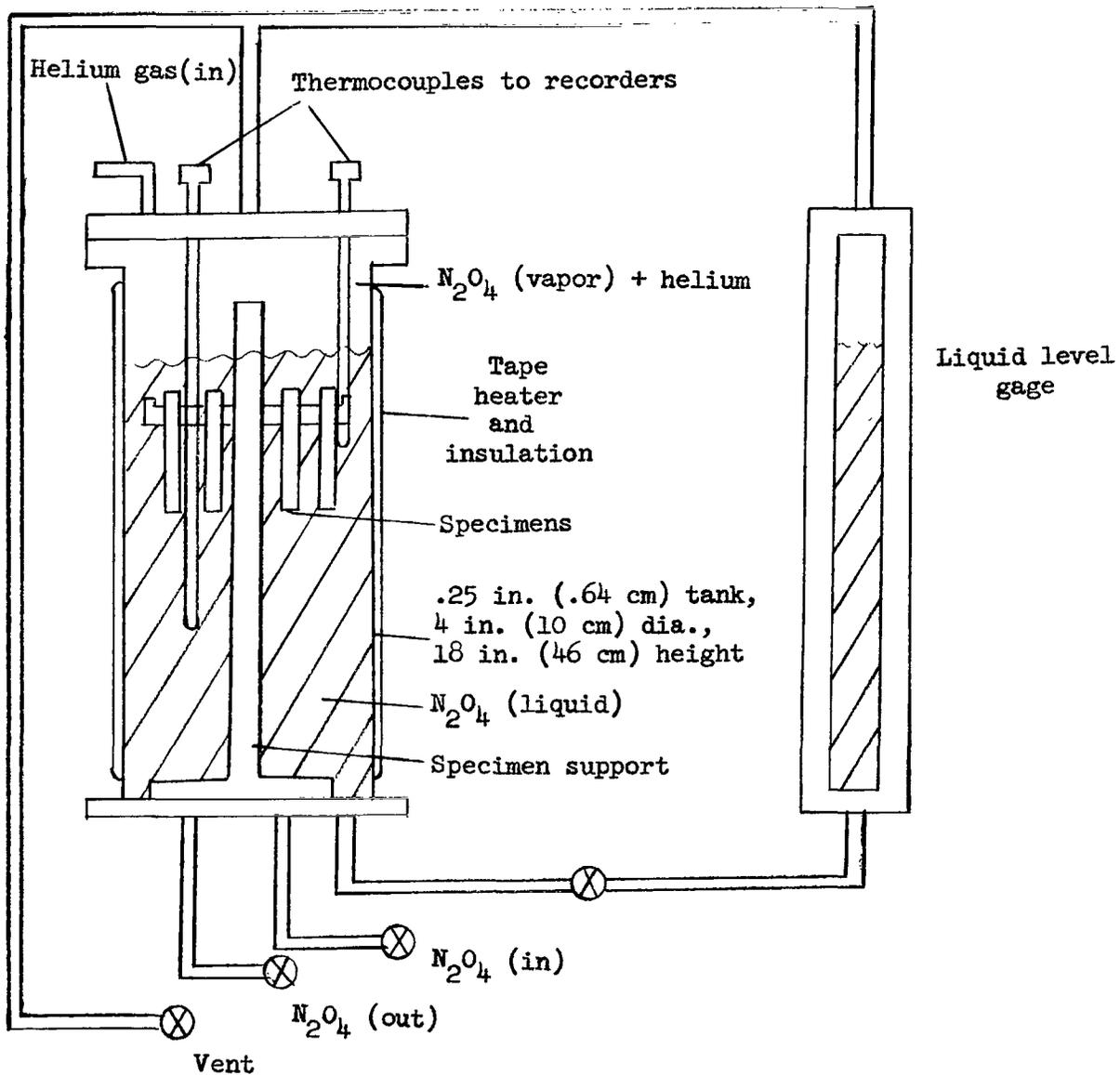


Figure 4.- Sketch of corrosion specimen test chamber.

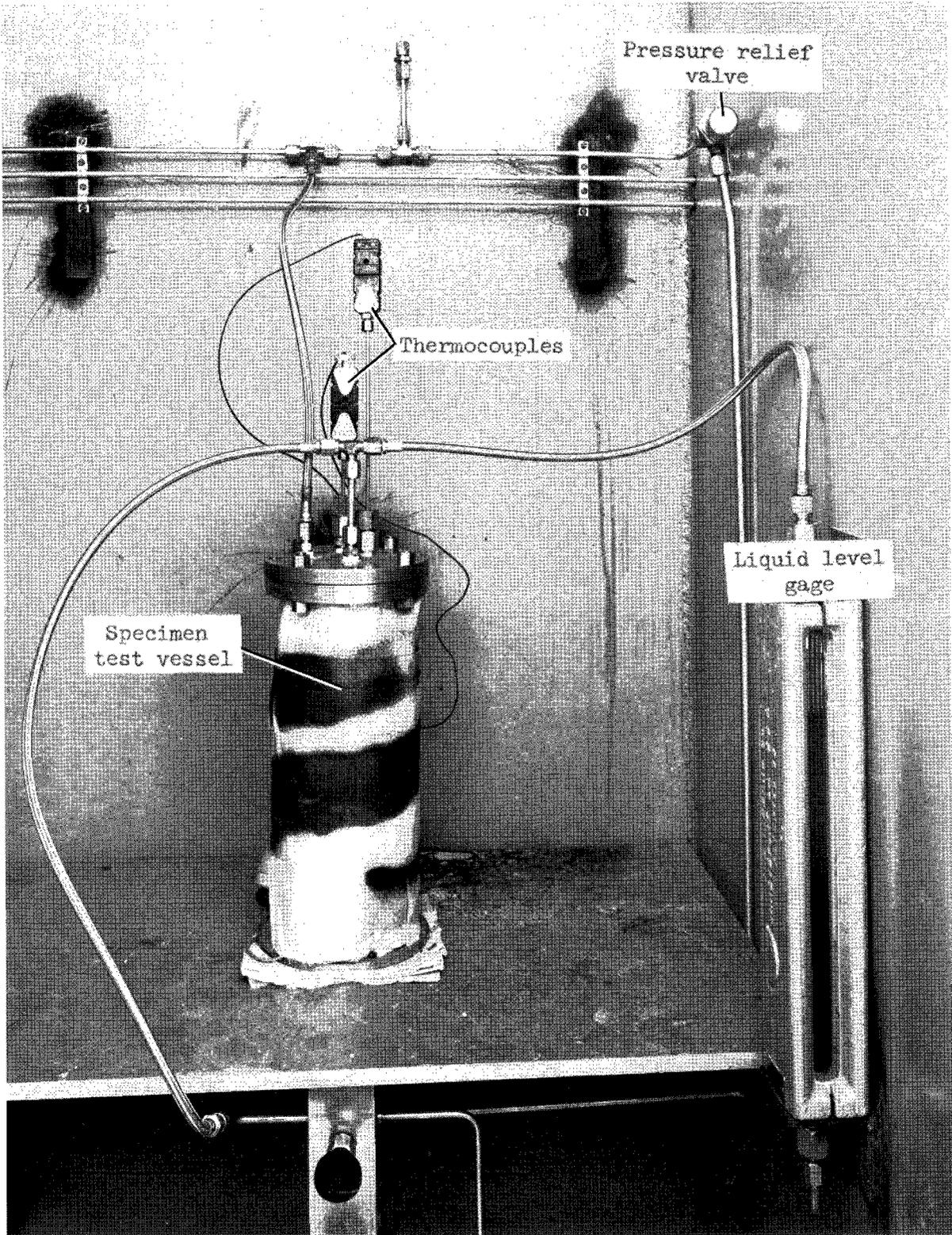


Figure 5.- Test setup for stress-corrosion tests of small specimens in  $N_2O_4$ .

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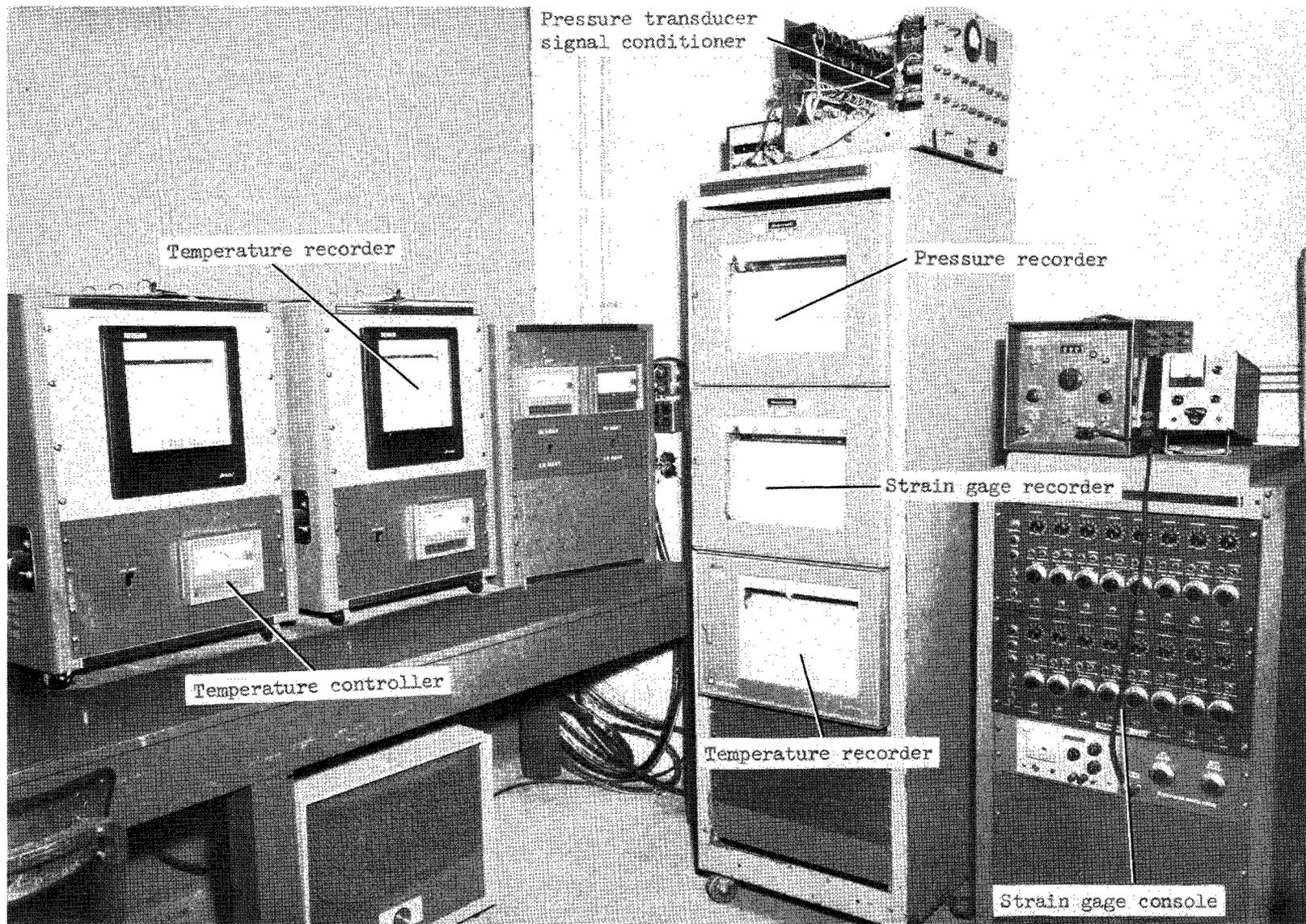


Figure 6.- Instrumentation for stress-corrosion tests.

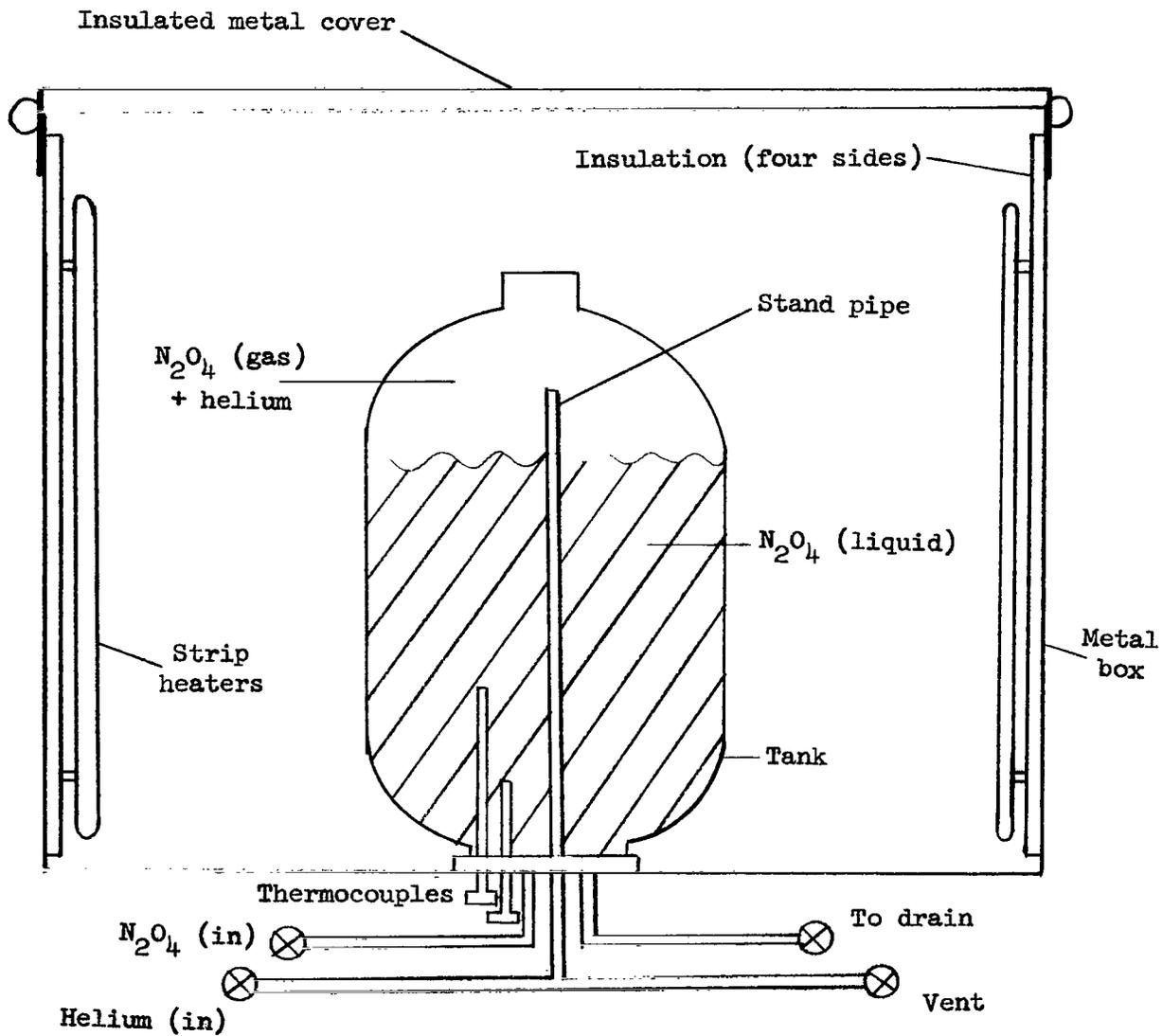


Figure 7.- Sketch of tank test setup.

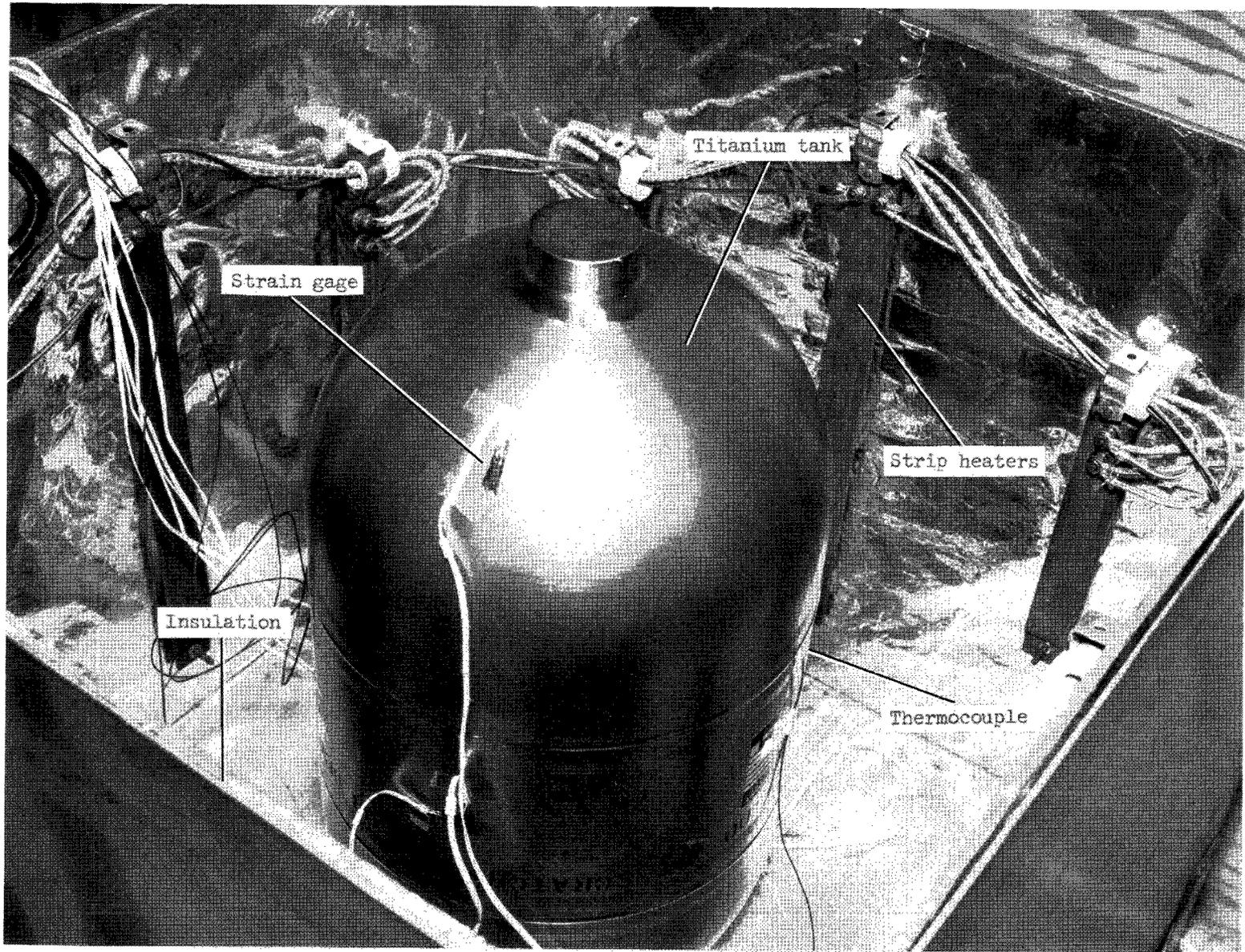


Figure 8.- Titanium-alloy tank in metal box. Insulation, strain gages, and thermocouples.

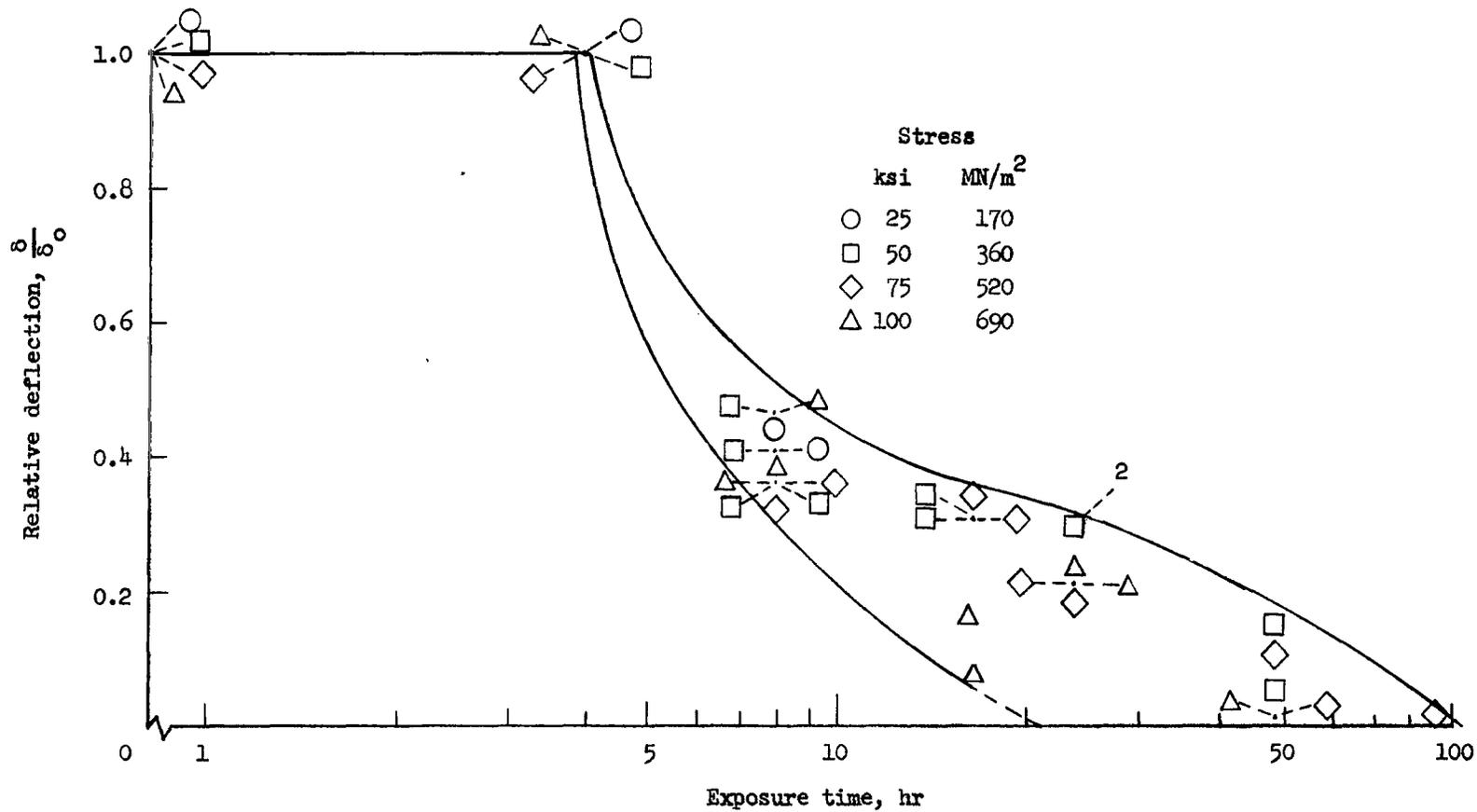


Figure 9.- Effect of exposure time on Ti-6Al-4V titanium-alloy self-stressed specimens in N<sub>2</sub>O<sub>4</sub> at 165° F (345° K). Oxidizer A.

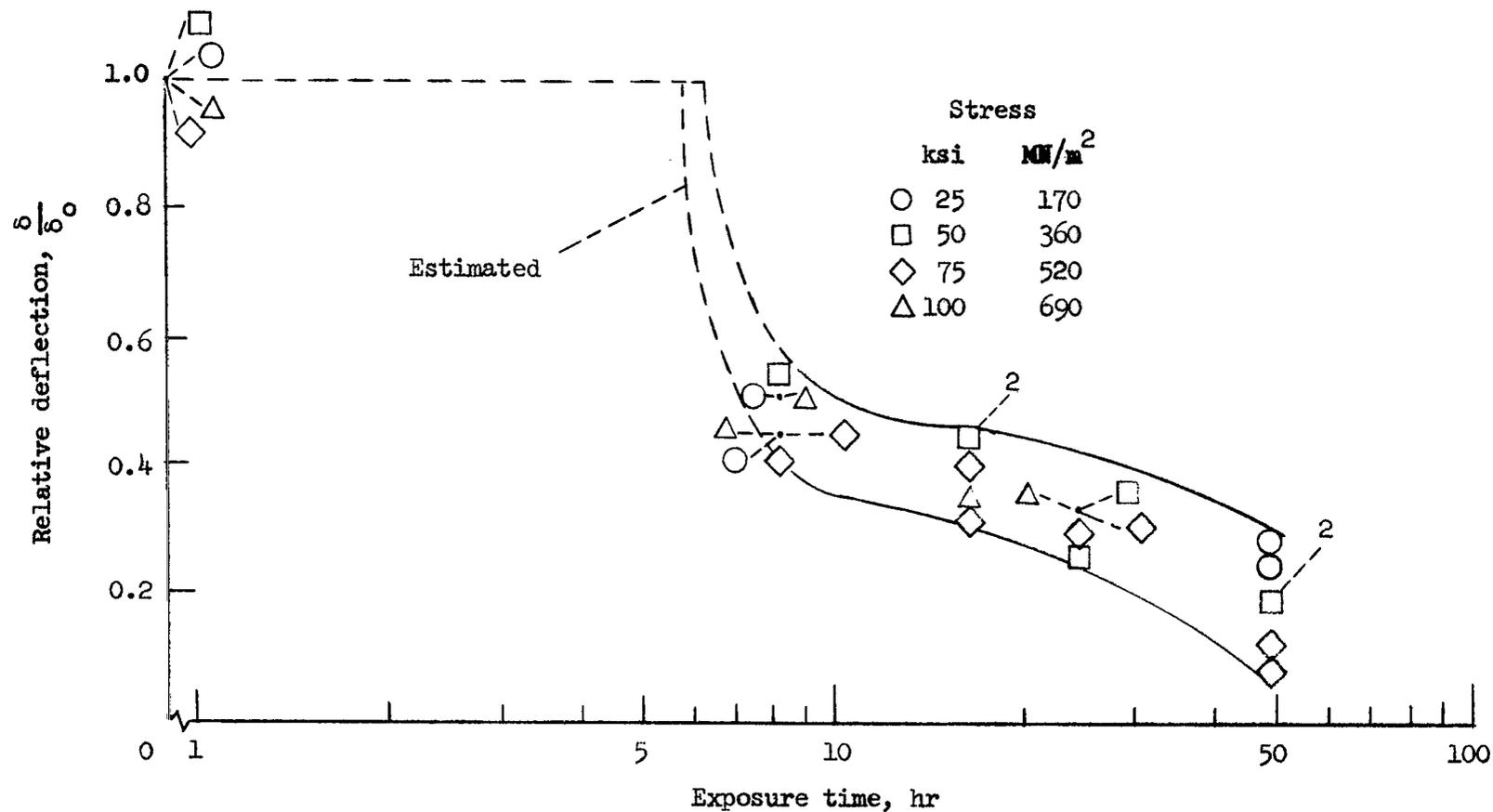


Figure 10.- Effect of exposure time on Ti-6Al-4V titanium-alloy self-stressed specimens in  $\text{N}_2\text{O}_4$  at  $145^\circ\text{ F}$  ( $335^\circ\text{ K}$ ). Oxidizer A.

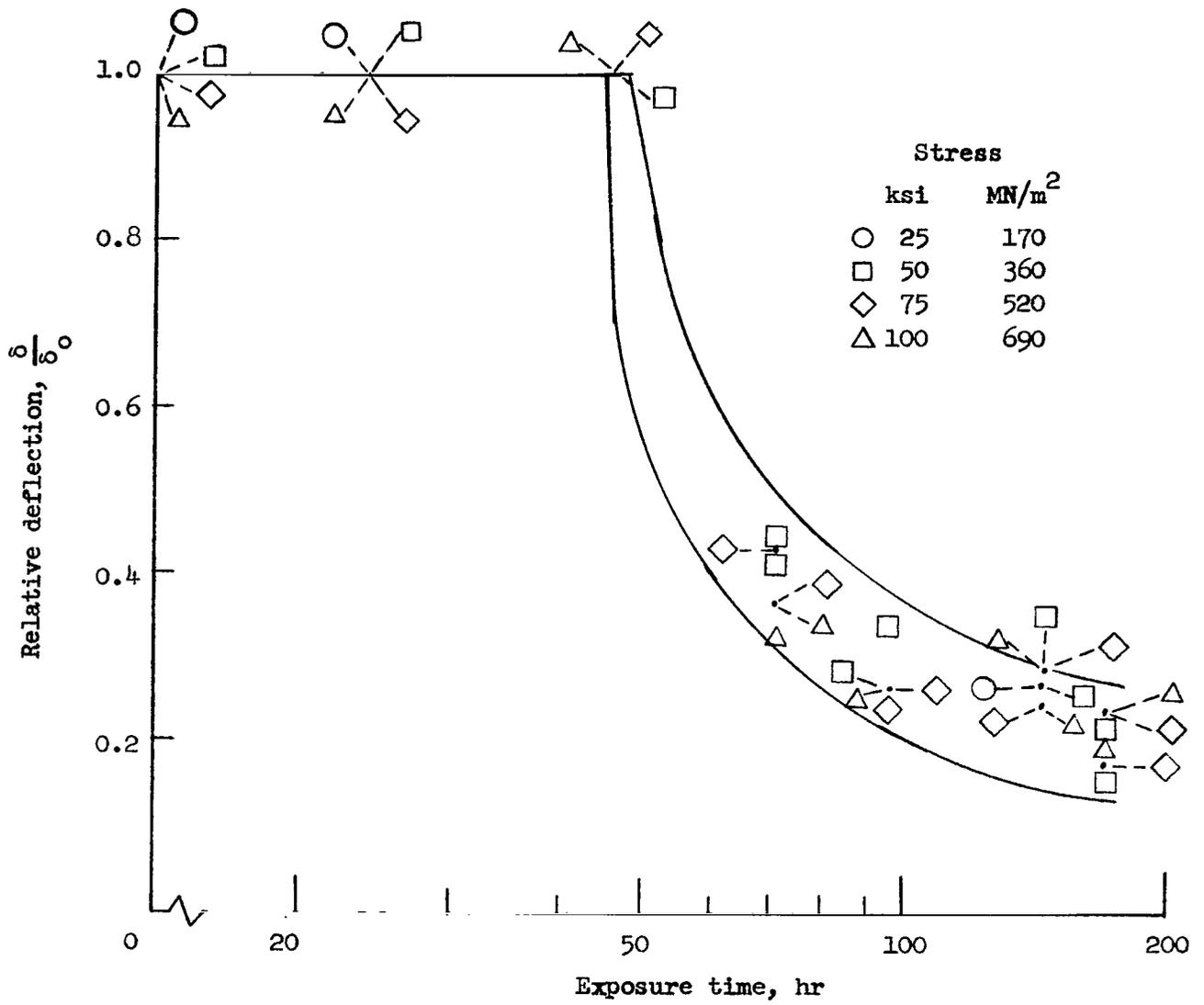


Figure 11.- Effect of exposure time on Ti-6Al-4V titanium-alloy self-stressed specimens in  $N_2O_4$  at  $105^\circ F$  ( $315^\circ K$ ). Oxidizer A.

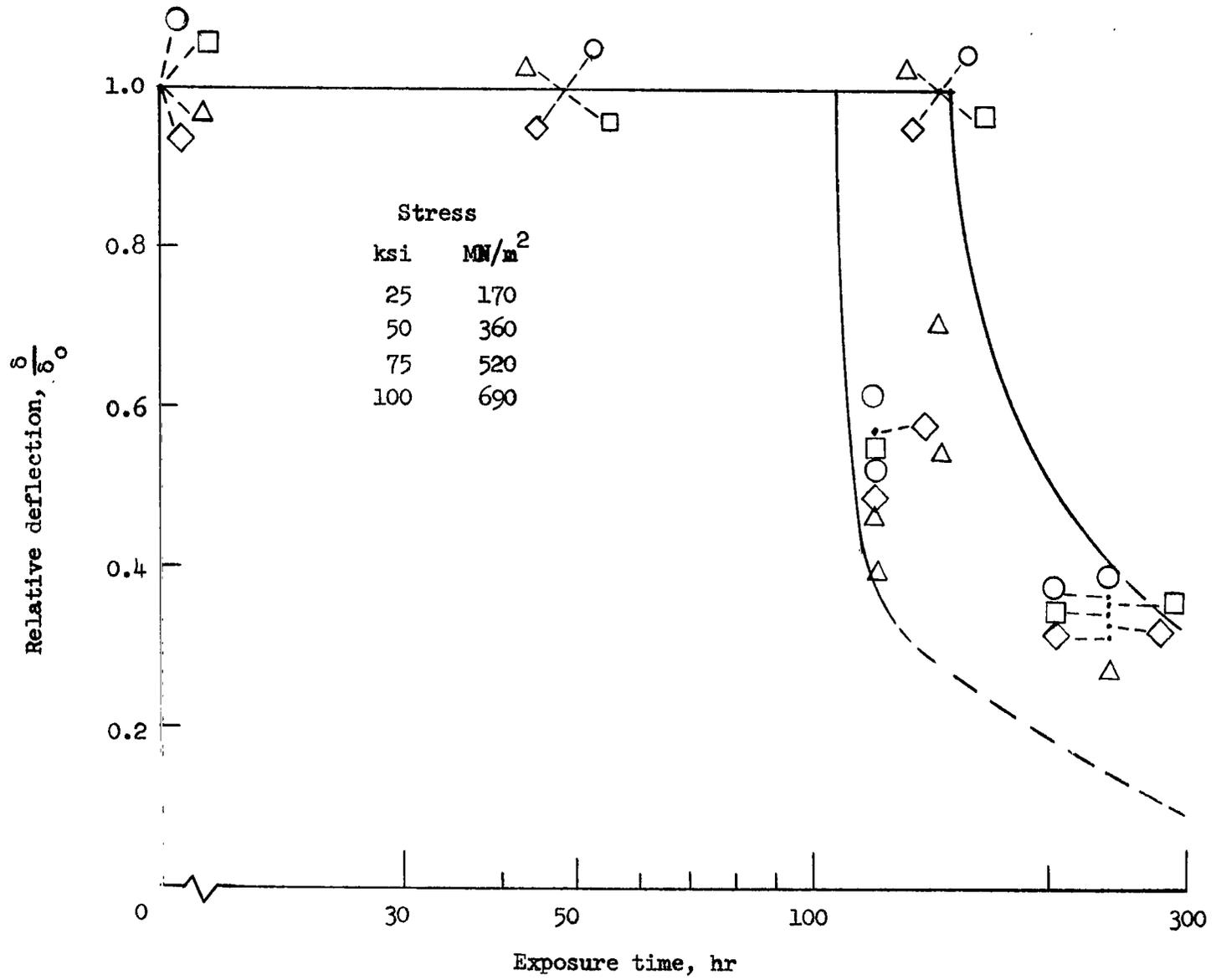
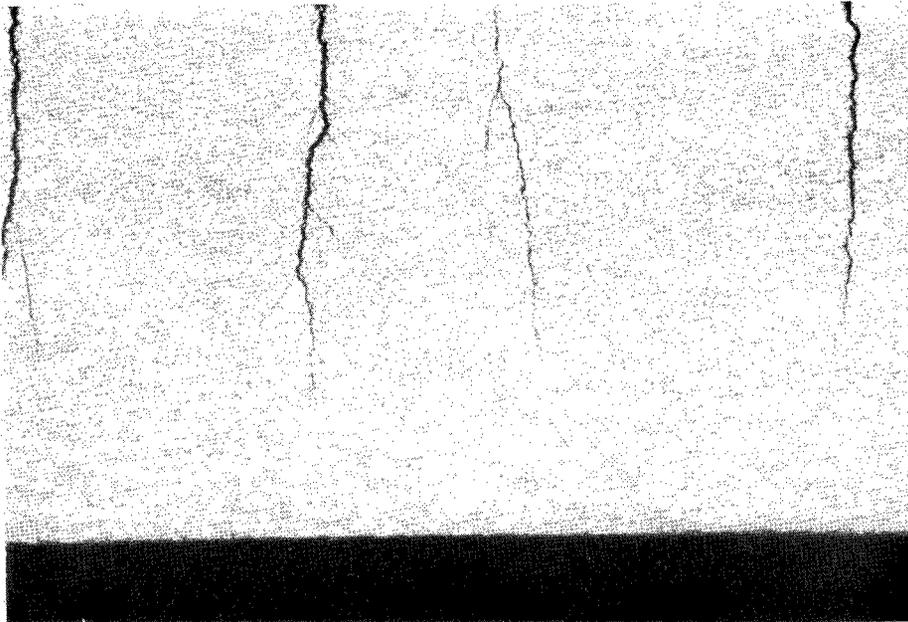


Figure 12.- Effect of exposure time on Ti-6Al-4V titanium-alloy self-stressed specimens in N<sub>2</sub>O<sub>4</sub> at 85° F (300° K). Oxidizer A.



75X



500X

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Figure 13.- Microstructure of Ti-6Al-4V titanium-alloy specimen showing stress-corrosion cracks after 8 hours exposure at 165° F and 100 ksi (345° K and 690 MN/m<sup>2</sup>) stress in N<sub>2</sub>O<sub>4</sub>.

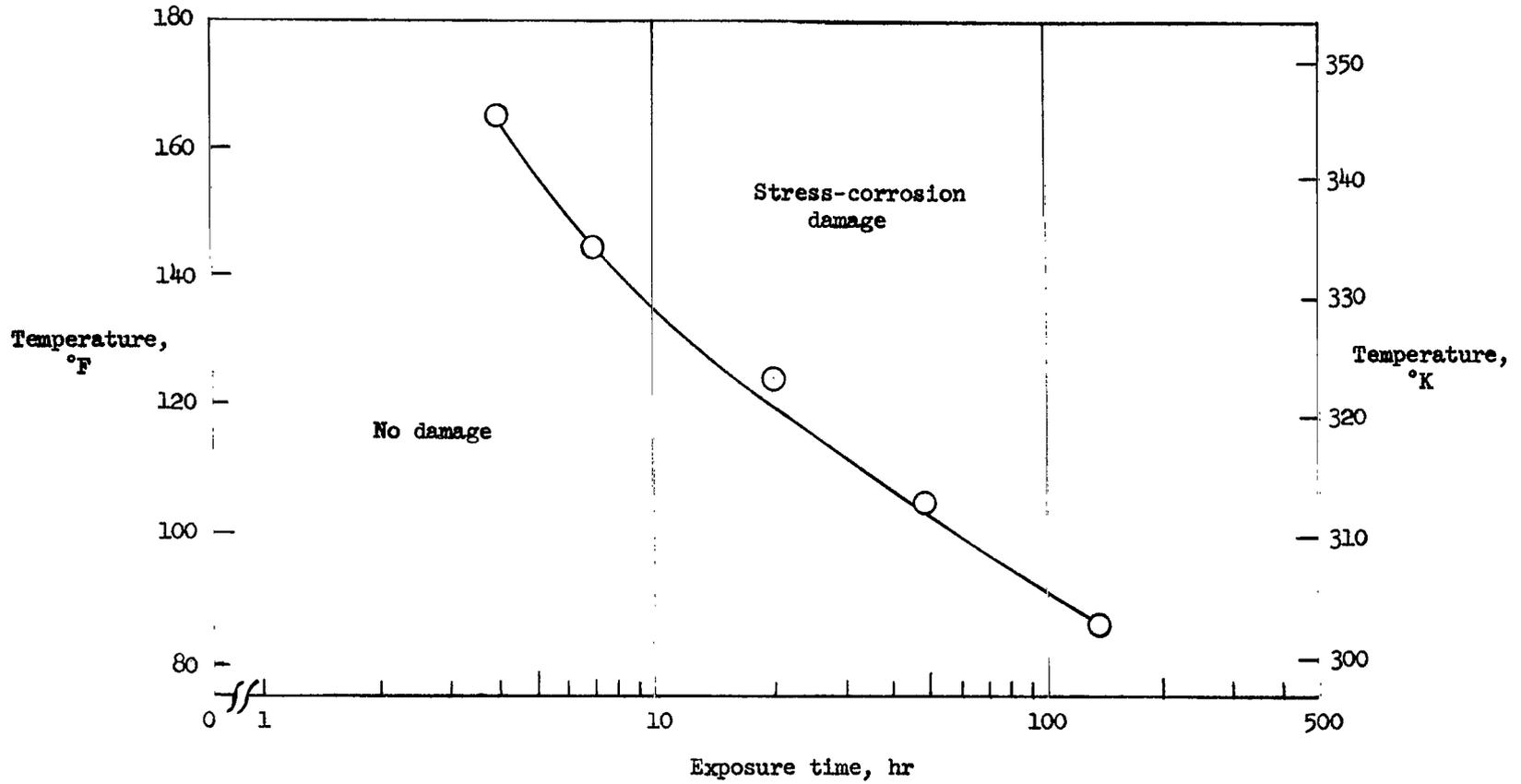


Figure 14.- Stress-corrosion damage boundary for Ti-6Al-4V titanium alloy exposed in  $N_2O_4$ . Oxidizer A.

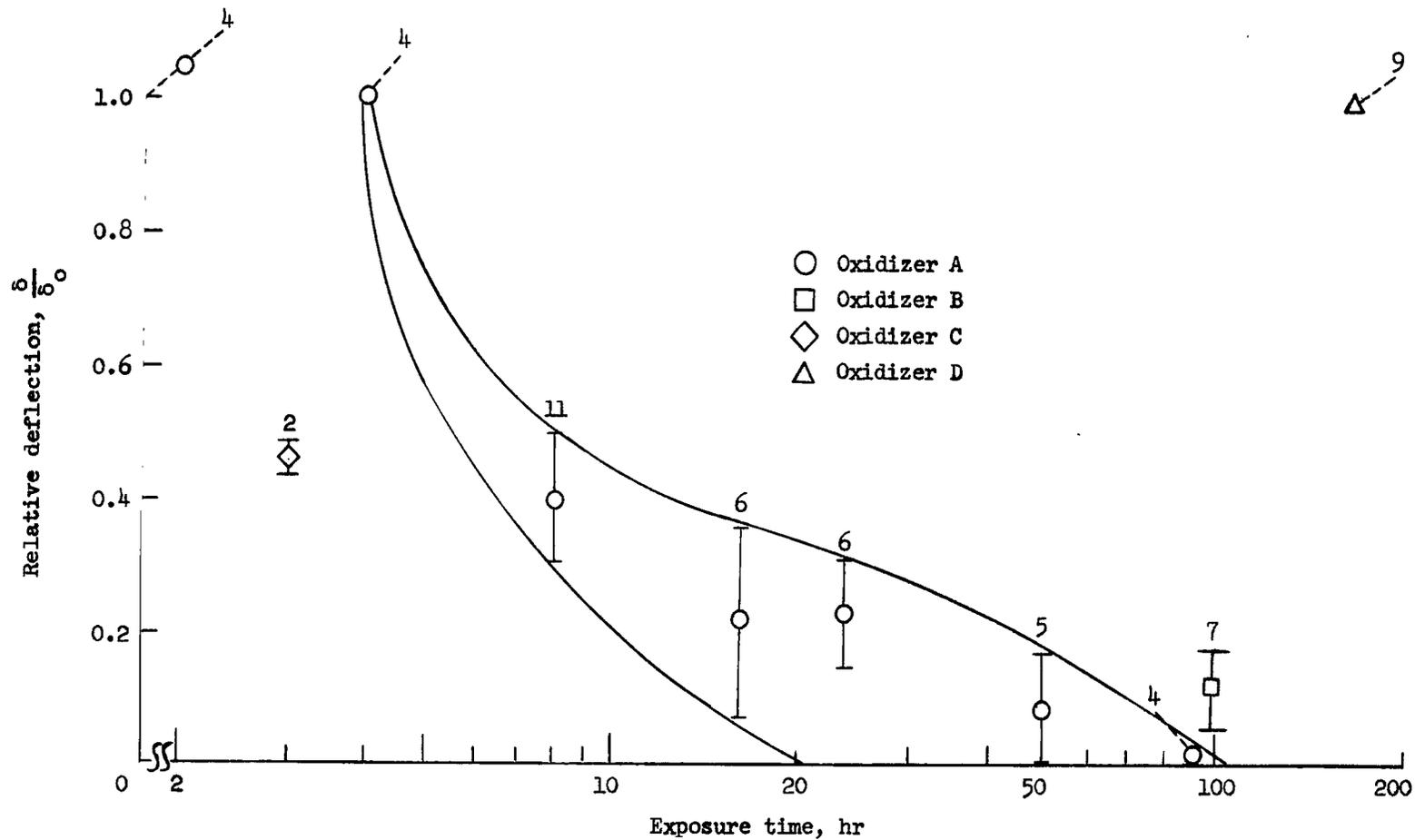


Figure 15.- Effect of variation in composition of  $N_2O_4$  on stress corrosion of Ti-6Al-4V titanium alloy at 165° F (345° K). See table II for composition of oxidizers.

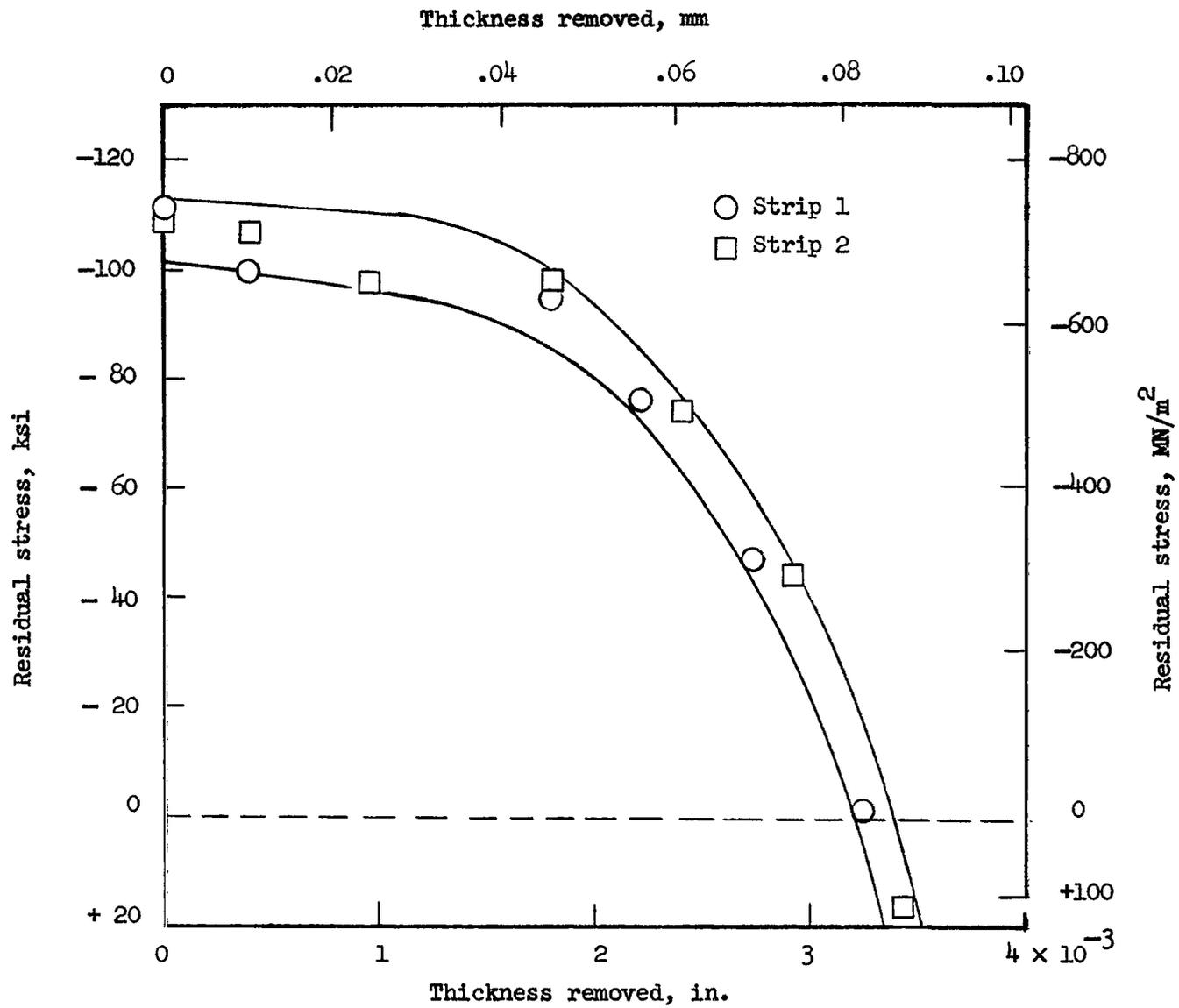


Figure 16.- Residual stress distributions for two peened Ti-6Al-4V titanium-alloy test strips. Minus sign indicates compressive stress; plus sign indicates tensile stress.

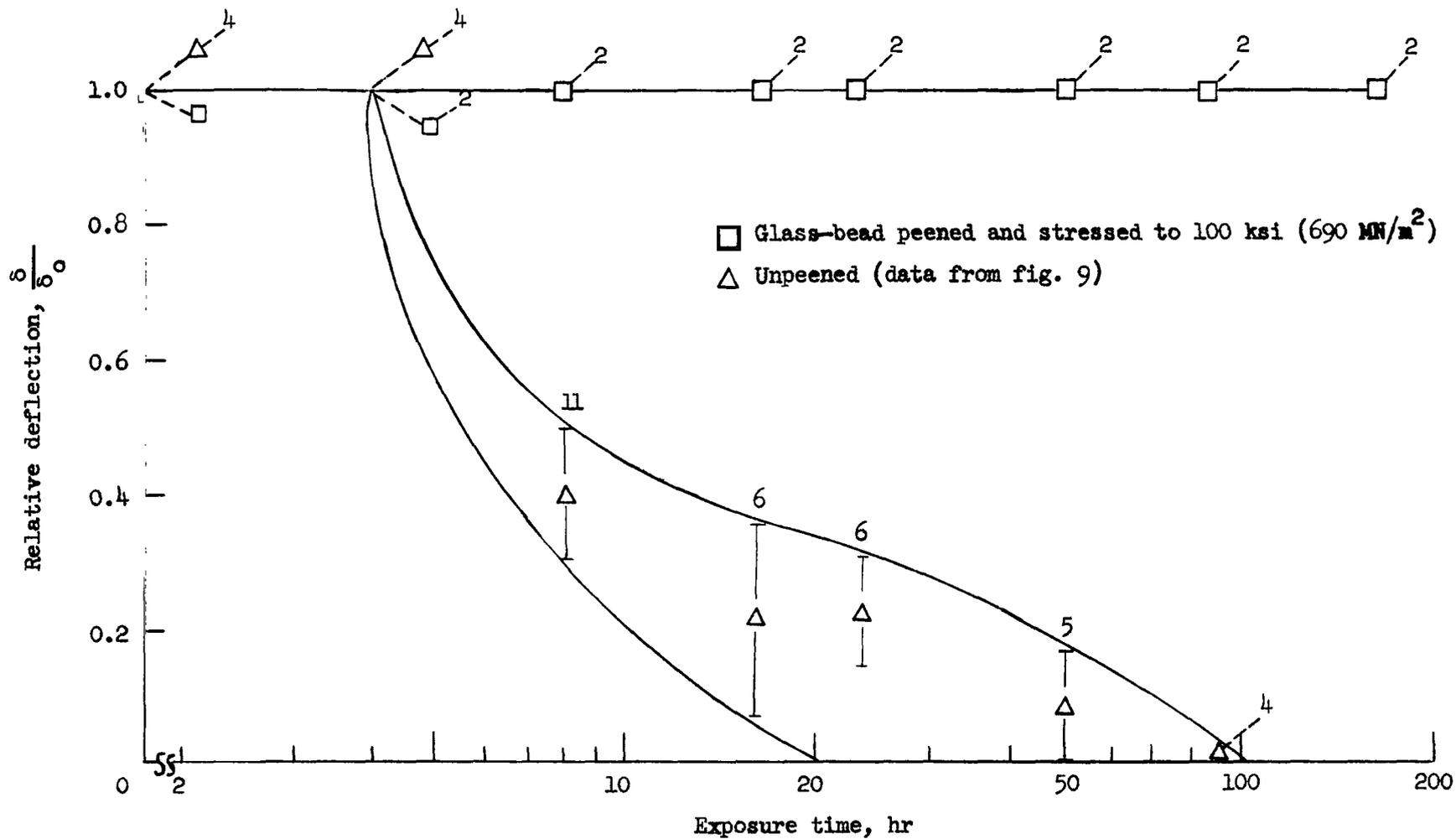


Figure 17.- Effect of exposure on Ti-6Al-4V titanium-alloy peened and unpeened specimens in N<sub>2</sub>O<sub>4</sub> at 165° F (345° K), Oxidizer A.

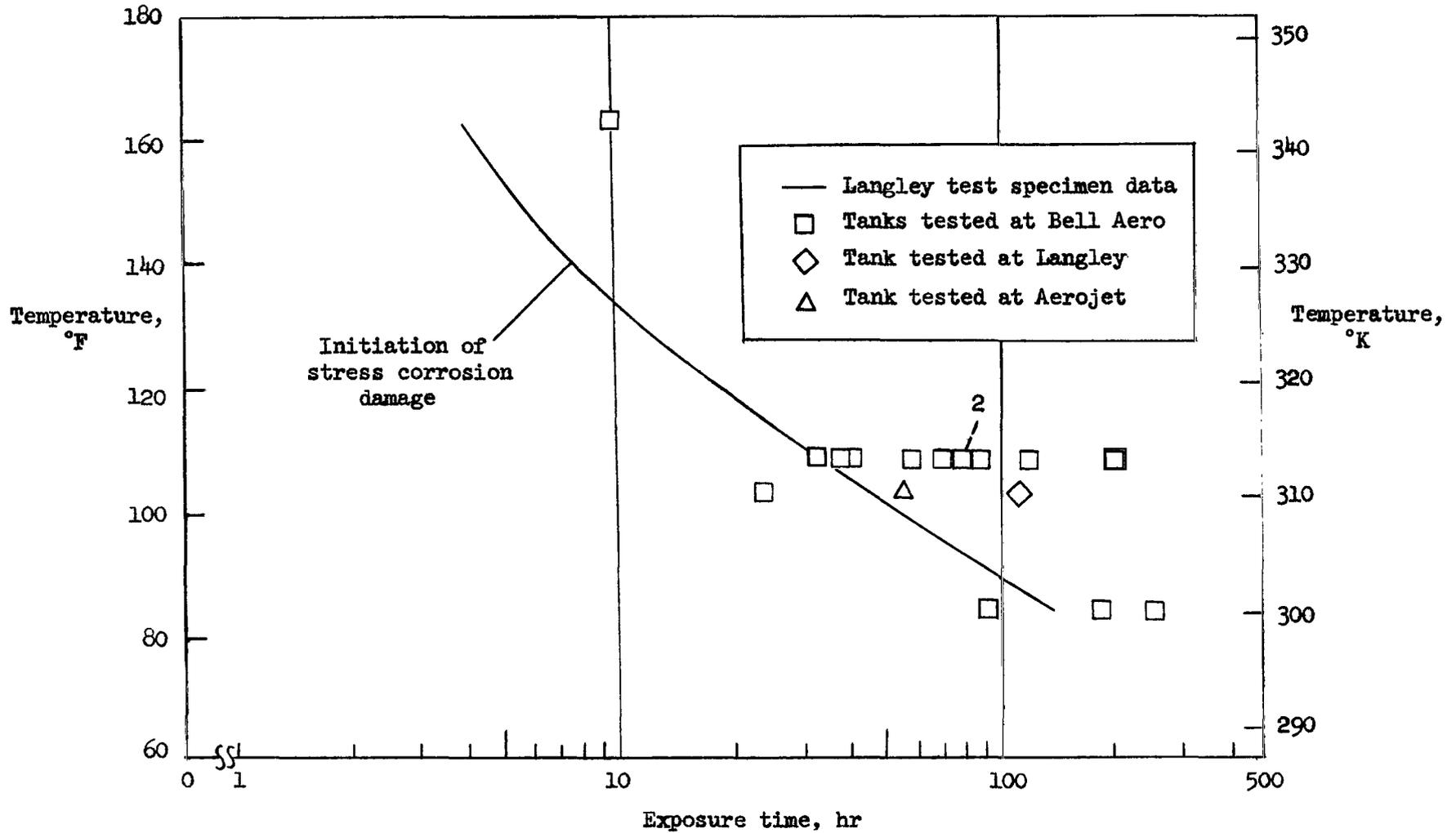


Figure 18.- Correlation between crack initiation of small stress-corrosion specimens and failure of tanks of Ti-6Al-4V titanium alloy after exposure in  $N_2O_4$ . Oxidizer A.

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